

(12) PATENT ABRIDGEMENT (11) Document No. AU-B-20823/83
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 568609

(51)4 International Patent Classification

C08F 283/00 B32B 017/10 C03C 027/12 C08F 002/50
C08J 005/12

(21) Application No. : 20823/83 (22) Application Date : 31.10.83

(30) Priority Data

(31) Number (32) Date (33) Country
8231736 05.11.82 GB UNITED KINGDOM

(43) Publication Date : 10.05.84

(44) Publication Date of Accepted Application : 07.01.88

(71) Applicant
DELTAGLASS S.A.;

(72) Inventor
PIERRE CHEVREUX
CHRISTIANE ALBERTINE REBENDER CHEVREUX

(74) Attorney or Agent
SPRUSON & FERGUSON

(54) Title
RADIATION CURABLE ACRYLATE URETHANE COMPOSITION

(56) Prior Art Documents
20822/83 C08F

(57) Claim

1. A radiation-curable liquid adhesive composition for glass, and which is especially suitable for bonding glass to plastics materials, said composition being of the kind comprising urethane acrylate in a liquid $\alpha\beta$ -ethylenically unsaturated diluent and characterised in that the urethane acrylate comprises (i) a first urethane acrylate component^{os} which ~~is formed at least~~ ^{at least 50% is formed} mainly of material having a molecular weight (M_N) above 1500, is oligomeric and has a functionality in the range of 1.7 to 2.3, and (ii) ~~an effective amount~~ ^{at least 0.5% based on the total weight of component (i) and component (ii)} of a second urethane acrylate component which has a functionality of at least 3 and a molecular weight (M_N) above 1200, said component (ii) forms a minor amount, by weight, of the total weight of component (i) and component (ii), and the polyisocyanate material from which each of components (i) and (ii) is derived is mainly or wholly polyisocyanate in which the isocyanate groups are attached to aliphatic carbon atoms.

-1-

RADIATION-CURABLE ADHESIVE COMPOSITIONS

ABSTRACT

A radiation-curable composition suitable for use as an adhesive for bonding glass, and in particular for the production of clear glass laminates, and of the kind comprising a urethane acrylate material in an α , β -ethylenically unsaturated diluent therefor, wherein the urethane acrylate material comprises a first component which is generally difunctional and a second component which has a functionality of at least about 2 and a molecular weight M_n above 1200.

10

transparent, preferably have a refractive index at least close to that of glass, exhibit adequate water- or moisture-resistance and be resistant to aging in sunlight. Further, since for many intended end uses it is desirable that at least one of the layers of the laminate is an organic glass such as methacrylate or polycarbonate or that a plastics foil such as of vinyl chloride polymer be provided between two glass sheets (one or both of which may be of organic glass), it is also desirable for the composition to bond well to certain plastics materials, especially those that are available as transparent sheets or film.

Much effort has been expended over the last 10 - 15 years in developing suitable compositions and a very wide variety of resinous components and diluent compositions has been proposed. One group of resins that has attracted particular interest comprises those which contain urethane groups and particular examples of these are the compounds obtainable by reacting a polyol with a polyisocyanate to form a preferably oligomeric urethane intermediate having terminal hydroxy and/or isocyanate groups and reacting the intermediate with an α,β -ethylenically unsaturated compound having a group which is reactive with a hydroxy or isocyanate group as appropriate. Where the unsaturated compound contains a carboxylic group attached to a carbon atom of the α,β -ethylenically unsaturated group, i.e., contains the group

urethane acrylate which has a functionality of at least about 3 and a molecular weight M_N above 1200.

Functionality as used herein with respect to urethane acrylates relates to the number of $\alpha\beta$ -ethylenically unsaturated groups per molecule.

According to the present invention there is provided a radiation-curable liquid adhesive composition for glass, and which is especially suitable for bonding glass to plastics materials, said composition being of the kind comprising urethane acrylate in a liquid $\alpha\beta$ -ethylenically unsaturated diluent and characterised in that the urethane acrylate comprises (i) a first urethane acrylate component^{0.5}_N ^{at least 10% is formed} which ~~is formed at least~~ mainly of material having a molecular weight (M_N) above about 1500, is oligomeric and has a functionality in the range of about 1.7 to about 2.3, ^{at least 0.5% based on the total weight of component (i) and component (ii)} and (ii) ~~an effective amount~~ of a second urethane acrylate component which has a functionality of at least about 3 and a molecular weight (M_N) above about 1200, said component (ii) forms a minor amount, by weight, of the total weight of component (i) and component (ii), and the polyisocyanate material from which each of components (i) and (ii) is derived is mainly or wholly polyisocyanate in which the isocyanate groups are attached to aliphatic carbon atoms.

By generally difunctional is meant that component (i), which may be a simple urethane acrylate or a mixture of urethane acrylates, has a functionality of about 2, i.e. from about 1.7 to about 2.3 preferably about 1.8 to about 2.2.

Urethane acrylates are notionally obtainable by the reaction of a polyol and a polyisocyanate to form an intermediate, which preferably is oligomeric in nature and which



The polyol material, which may be one or a mixture of polyols, from which component (i) is derived is preferably at least mainly, and more preferably entirely or substantially entirely, polyether polyol; i.e. the oligomeric chains are formed of repeating ether units. Examples of such polyols are oligomers of epoxides, especially ethylene oxide, propylene oxide or mixtures thereof. Best results are obtained when the oligomeric chains of the polyol material are free or substantially free of linking groups other than ether, especially ester groups the presence of which appears to have a detrimental effect on water resistance.

The polyol material will be largely or wholly diol in order to achieve the desired functionality in component (i).

The polyisocyanate material, which may be one or a mixture of polyisocyanates, from which component (i) is derived may include aromatic polyisocyanates, e.g. as in phenylene diisocyanates, toluene diisocyanates and bis(isocyanatoaryl)-alkanes, but is preferably at least mainly, and more preferably entirely or substantially entirely, polyisocyanate in which the isocyanate groups are attached to aliphatic carbon atoms. The inclusion of isocyanate groups attached to aromatic carbon atoms appears to adversely affect the water resistance and/or u.v. resistance of the composition. The polyisocyanate material will be largely or wholly diisocyanate to achieve the desired functionality in component (i). Examples of aliphatic

composition does not appear to be obtained. Preferably the molecular weight is at least about 1300, more preferably at least about 1500 and most preferably at least about 2000.

Contrary to the case for component (i), the polyol material from which component (ii) is derived, and which may be one or a mixture of polyols, may be at least mainly polyester polyol; i.e. polyol wherein the oligomer chains comprise repeating ester groups. In fact, very good results are obtained when the polyol is derived from lactone, especially a caprolactone by which is meant a lactone having 7 atoms, including the oxygen atom, in the lactone ring, the free valencies of the ring carbon atoms generally being satisfied by hydrogen atoms although substitution by lower alkyl groups having one to four carbon atoms may also be tolerable.

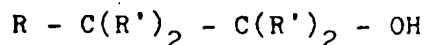
As in component (i), the polyisocyanate from which component (ii) is derived, and which may be one or a mixture of polyisocyanates, is preferably at least mainly polyisocyanate in which the isocyanate groups are attached to aliphatic carbon atoms. Examples are as given above for component (i).

To obtain the desired functionality of component (ii), at least one of the polyisocyanate and polyol will contain material having at least three active, i.e. -NCO or -OH, groups, respectively. Polyols having three or more hydroxy groups may be obtained, for example, by polymerising a lactone in the presence of a compound having three or more active hydrogen atoms e.g. a

also be included, if desired. Examples are vinyl ethers, nitriles of unsaturated acids, esters of unsaturated acids and saturated alcohols and esters of saturated acids and unsaturated alcohols. Such compounds may also include other polar groups such as hydroxy, amino and urethane groups, e.g. as in hydroxyalkyl, N,N-dialkylaminoalkyl and N-carbamoylalkyl esters of α/β -ethylenically unsaturated acids.

Where good water-resistance and/or u.v.-resistance is desired, a preferred class of monomer for use in conjunction with acrylic acid in the diluent comprises monoesters of acrylic acid. However, as an increase in the molecular weight of the alcohol from which the monoester is derived tends to reduce the compatibility of the composition and adversely affect clarity, it is preferred that the monoester is derived from an alkanol having from 1 to 6 carbon atoms or a substituted derivative thereof preferably containing only carbon, hydrogen and oxygen atoms.

Particularly preferred are the monoesters of alcohols having the structure



where R is -H, -OH or a monovalent organic group containing atoms selected only from carbon, oxygen and hydrogen, and having not more than 4 atoms in a chain attached to the free valency, and each R' is individually selected from -H and -CH₃ or R and R' together form a divalent group containing atoms selected from carbon, oxygen and hydrogen. Diluents containing such monoesters

10 preferred that the monoester does not exceed 400% by weight of the acrylic acid, by weight. It has also been observed that if the monoester is present in substantial amounts, the bond strength tends to be significantly reduced. Accordingly the monoester is preferably employed in amounts of about 10% to 65 or 70%, more preferably about 12½% to 60% based on the combined weight of monoester and acrylic acid. The preferred amount may vary with the nature of the monoester and the composition of the urethane acrylate but in general it is desired that the bond strength of the adhesive is at least 300 g/cm, preferably at least 500 g/cm and most preferably at least 1000 g/cm, and that the bond has a "driness", determined as described below in the description of Examples 4 to 11, of at least "B", and preferably "C" and the most preferred range is about 14% or 18% to about 30% or 35% of monoester based on the combined weight of the monoester and acrylic acid in the diluent.

20 The diluent may, if desired, also include one or more, α,β -ethylenically unsaturated compounds in addition to the acrylic acid and specified acrylate, e.g. to adjust the viscosity or reactivity of the composition. Particular examples of such additional components are other α,β -ethylenically unsaturated acids e.g. methacrylic acid or α -cyanoacrylic acid; acrylates other than the specified acrylates, e.g. aminoacrylates, monomeric urethane acrylates and esters of acrylic acid with alkanols having 8 or more carbon atoms; methacrylates;

the total composition. Preferably, therefore, such compounds are employed in amounts of less than about 5%, preferably less than about 2.5% by weight of the composition. Most preferably, the composition is free or substantially free of such compounds.

The composition may also, if desired, contain a resinous or polymeric material in addition to the urethane acrylate. Preferably said material is at least substantially saturated e.g. as in epoxy resins, especially those derived from epichlorhydrin and bis-phenols such as bis-phenol A. However the use of unsaturated resins such as $\alpha\beta$ -ethylenically unsaturated polyesters is not excluded. Such additional resinous material will not normally form more than 50% by weight of the total composition, however.

The inclusion of balsamic resins is particularly preferred as they increase the resistance of the cured compositions to yellowing with age, even at quite low concentrations such as 2.5% by weight of the total composition. Examples of such resins are the high molecular weight alcohols obtained by the hydrogenation of resinic acids and described generically as hydroabietyl alcohols, such as those marketed under the Trade Name "ABITOL", and esters, such as the triethylene glycol esters and hydrogenated methyl esters, of colophony, such as those marketed under the Trade Names "HERCOLYN" and "STAYBELITE". In general sufficient protection is obtained with the use of 5% of the resin and little further benefit is obtained by exceeding 10% although larger amounts may be used if desired.

the photoinitiator should not introduce discolouration into the composition. Good reactivity, colour, water-resistance and adhesion are obtained using benzophenone, but many possible alternatives are suggested in the art. The photoinitiator is preferably employed in an amount of about 0.5 to about 10% by weight of the basic composition, most preferably about 1 to about 5%.

10 The u.v. irradiation period required to achieve the polymerisation of the adhesive is directly related to the time after which the minimum dose of radiation of proper wavelength has been absorbed by the adhesive layer. It therefore depends on the spectral distribution of the source, the power thereof, the distance thereof from the substrate to be irradiated and the optical transmission of that layer of the substrate which must be penetrated by the light before reaching the adhesive itself. Thus, glass and synthetic resins all have some significant extinction coefficient in the u.v. range and, consequently, the irradiation duration must be adapted to the optical properties of each material used.

20 As u.v. irradiation sources, any having an emission spectrum largely comprised above 0.3μ is convenient, e.g. mercury vapor lamps. One or more lamps of 20 W to about 10 KW can be used, e.g. a 2 kW lamp of type HTQ7 made by PHILIPS or a high-pressure mercury vapor lamp giving 80 W/cm made by HANOVIA. Argon or krypton lamps can also be used.

By means of the invention, it is possible to obtain a u.v.-radiation curable adhesive composition comprising urethane acrylate and an $\alpha\beta$ -ethylenically unsaturated diluent therefor, and having a very desirable combination of viscosity in the uncured state, reactivity in terms of time to cure when exposed to a source of u.v-radiation, and bond strength, water-resistivity, u.v.-resistivity. colour and clarity when cured. In particular, there can be obtained compositions having a viscosity of 1200 cp or less, measured using a Brookfield LV viscometer with a No. 1 spindle at 6 rpm at 20°C, and a cure time, as herein defined, of 30 seconds or less, and which cures to a clear and colourless adhesive layer having a bond strength of at least 500 g/cm, a water-resistance of at least 4 and u.v.-resistance of 0, where bond strength, water-resistance and u.v.-resistance are all as defined herein.

The invention is now illustrated by the following Examples in which all parts are expressed by weight unless otherwise indicated.

In these Examples, water resistance, u.v. resistance, bond strength and cure time were measured as follows:

Water Resistance: an excess of the composition is applied to one face of a 50 x 25 x 4 mm glass plate. A second glass plate of identical size is then pressed on to the coated surface and the excess adhesive expressed from the edges of the assembly is wiped off. After curing, the assembly is immersed in boiling water for

from the degree to which the adhesive layer has become discoloured after 63 hours exposure and is recorded on the scale 0 - 5 where 0 means there has been no observable colour change, 5 means a deep yellow colour has developed and numerals 4 to 1 relate to progressively lighter yellow colours.

Bond strength was measured by a Peel Test according to ASTM D 1876-69. A 4 x 40 x 100 mm glass plate is bonded to a 40 x 165 mm sample of pvc film, e.g. Storey's VIBAK VB 24, using a sample of the composition. The pvc film is then cut to produce a centrally disposed 25 mm wide band and the lateral bands are removed to avoid any edge effects. The central pvc band is then peeled from the glass strip at 180° and a parting speed of 30 cm/minute using an Instron or similar machine. The resistance, measured in g/cm is a measure of the bond strength.

Cure time. Time taken to cure the composition when employed as a layer between the pvc film used in the 'Bond Strength' test and a 3 mm thick sheet of float glass and irradiated through the glass sheet using a 1 kw u.v. radiation source having a wavelength of approximately 10 cm and spaced 40 cm from the surface of the glass sheet.

The urethane acrylates employed in the following Examples are as follows:

Ebecryl 230, a urethane acrylate marketed by U.C.B. of Belgium, described as having a molecular weight M_N of about 5000 and an average functionality of 2 and found by analysis to contain

weight material consisting largely of MCEA.

Genomer T-1600, marketed by Rahn S.A. of Switzerland and described as oligomeric urethane acrylate free of diluent and having a molecular weight M_N of about 1600 and about three acrylate groups per molecule, on average, and shown by analysis to be derived from caprolactone-derived polyol, isocyanate material including hexamethylene diisocyanate, and acrylic acid.

10 All the compositions described in the Examples are curable within a few seconds to tough flexible transparent colourless and generally clear films having a refractive index equal or very similar to that of glass.

Example 1

An adhesive composition was prepared from 57 parts of Ebecryl 230, 2 parts of Actomer X-117, 29 parts of acrylic acid, 9.5 parts of n-butyl acrylate and 2.5 parts benzophenone. The composition was clear, colourless and transparent and the results obtained were as follows:

Viscosity of uncured composition (measured on a Brookfield LV Viscometer at 20°C using a No. 1 spindle at 6 r.p.m.):

as formed : 700 cp

after 4 months storage in the dark : no change

Curing time : 25-30 secs

Bond strength : about 2100 g/cm

Water resistance : 3-4

U.V. resistance : 0

<u>Type of Laminated Glass</u>	<u>Average number of strikes required before ball passed completely through laminate</u>
A. 4 mm glass/0.76 mm interlayer/ 4 mm glass, sold commercially as "KINON"	5
B. 4 mm glass/0.76 mm interlayer/ 4 mm glass, sold commercially as "SIV"	4

10

In both the above cases, when the test was repeated at 45-50°C, the ball passed through the laminate on the first drop because of the loss of strength of the polyvinyl butyral interlayer at this temperature.

By way of comparison, a further composition was formed as above, but excluding the X-117; and laminates formed therefrom were subjected to the falling ball test. When the glass shattered under the impact, a larger proportion of the glass splinters and fragments so formed tended to become detached from the laminate. Moreover, the bond strength of the adhesive was significantly reduced.

20

Example 2

Results similar to those reported in Example 1 were obtained when the Actomer X-117 was used in amounts of 5 parts and 10 parts by weight, respectively.

311003 00003

Example	4	5	6	7	8	9	10	11
Acrylic Acid	38.5	33	27.5	24	18.5	14	9.5	0
n-Butyl Acrylate	0	5.5	11.0	14.5	20	24.5	29	38.5
Cure time (sec)	15-20	*	*	*	40-50	*	40-50	30
Bond strength (g/cm)	1300	1600	2400	2400	2000	600	400	nil
Water resistance	2	3.5	4.5-5	*	4.5-5	4	2.5	*
u.v. resistance	good	good	good	good	good	good	good	good

* not measured

A decrease in "driness" (or increase in "softness" or "suppleness") of the bond is normally accompanied by an increase in the performance in the "Falling Ball" test, described in Example 1, of glass/plastics interlayer/glass laminates formed from the composition; especially a reduction in the tendency (a) of the laminate to delaminate under impact and (b) of glass fragments to fall away when one or other of the glass layers is shattered under impact.

Examples 12 - 19

10 A series of formulations were prepared with 55.3 parts Ebecryl 230, 28.0 parts acrylic acid, 9.3 parts of another monomer, 2.5 parts of benzophenone and 4.9 parts of Actomer X-117. The nature of the monomer and the results obtained are set out in the Table below.

In Examples 13, 15, 17 and 19, there was evidence of a trace of incompatibility but insufficient to affect clarity significantly. At higher levels of these components in the diluent, however, significant incompatibility can occur.

Example 20

When Example 1 was repeated but with the Actomer X-117 present in an amount equal to that of the Ebecryl 230, by weight, the bond strength of the resultant adhesive was slightly lower at 1960 g/cm, cure time was about the same but the water-resistance was substantially reduced at 1.5. In a fifth experiment in which all the Ebecryl 230 was replaced by Actomer X-117, the water-resistance was still further reduced at 1.0, the cure time exceeded 2 minutes and the bond exhibited driness.

Example 21

An adhesive composition was prepared from 55.3 parts Ebecryl 230, 37.3 parts methacrylic acid, 2.5 parts benzophenone and 4.9 parts Actomer X-117. The water-resistance was high at 7 and the bond strength was 1700 g/cm but the cure time was nearly one minute.

Examples 22 - 30

Varying amounts of the combination of acrylic acid and n-butyl acrylate of the composition of Example 18 were replaced

Example 31

The composition of Example 18 was modified by the inclusion of 5 parts of a balsamic resin sold as ABITOL by Hercules NV of Netherlands. A sample of the formulation was then employed to fill the space between two 3 mm thick glass sheets spaced 0.75 mm apart and cured and the resultant laminate was exposed to the light of a 1 Kw high pressure mercury lamp. After 186 hours continuous exposure, the cured composition was still water-white. When the experiment was repeated using the formulation of Example 18, the cured composition turned a very pale straw colour after 186 hours exposure.

Examples 32 and 33

Example 31 was repeated but using 2.5 parts of balsamic resin (Example 32) and 10 parts of balsamic resin (Example 33). An improvement in aging was observed in Example 32 but the results were not quite as good as Example 31. In Example 33, the improvement over Example 31 was barely perceptible.

Examples 34 and 35

Example 31 was repeated but replacing the ABITOL with corresponding amounts of other balsamic resins, namely Staybelite Ester 3 (Example 34) and Hercolyn (Example 35), with the same results.

component (i) has a molecular weight M_N in the range of 3000 to 7000.

11. A composition as claimed in any one of claims 1 to 10 wherein component (i) forms from 50% to 99% by weight of total urethane acrylate in the composition.

12. A composition as claimed in any one of claims 1 to 11 wherein more than 50% the polyol material from which component (ii) is derived is polyester polyol.

13. A composition as claimed in claim 12 wherein the polyol material from which component (ii) is derived is derived from lactone.

14. A composition as claimed in claim 13 in which the lactone comprises caprolactone.

15. A composition as claimed in any one of claims 1 to 14 wherein more than 50% of the polyisocyanate material from which component (ii) is derived is polyisocyanate in which the isocyanate groups are attached to aliphatic carbon atoms.

16. A composition as claimed in any one of claims 1 to 15 wherein component (ii) forms from 0.5% to 30% by weight of the total urethane acrylate.

17. A composition as claimed in any one of claims 1 to 15 wherein component (ii) forms from 0.8% to 20% by weight of the total urethane acrylate.

18. A composition as claimed in any one of claims 1 to 15 wherein component (ii) forms from 1% to 15% by weight of the total urethane acrylate.

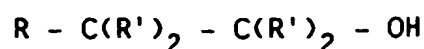
19. A composition as claimed in any one of claims 1 to 18 wherein the diluent includes acrylic acid.

20. A composition as claimed in any one of claims 1 to 19 wherein the diluent comprises acrylic acid and at least one monoester of acrylic acid.

21. A composition as claimed in claim 20 wherein said at least one monoester is derived from an alkanol having from 1 to 6 carbon atoms and substituted derivatives thereof.

22. A composition as claimed in claim 21 wherein said alkanol or substituted derivative thereof contains only carbon, oxygen and hydrogen atoms.

23. A composition as claimed in claim 21 wherein said at least one monoester is derived from an alcohol having the structure



which cures to a clear and colourless adhesive layer having a bond strength of at least 500 g/cm, a water-resistance of at least 4 and u.v.-resistance of 0, where bond strength, water-resistance and u.v.-resistance are all as defined herein.

36. A method of producing a clear glass laminate which involves bonding a first sheet of glass to a second sheet which is selected from glass sheets and clear plastics sheets using an adhesive, wherein as adhesive there is used a composition as claimed in any one of the preceding claims and the assembly of sheets with a layer of the adhesive composition therebetween is exposed to irradiation to cure the adhesive and bond the sheets together.

37. A method of producing a clear glass laminate in which one face of a clear plastics foil or film interlayer is bonded to a glass sheet and the other face is bonded to a second sheet which is selected from glass sheets and clear plastics sheets, wherein the bonding of at least said glass sheet to said interlayer is effected by means of an adhesive composition as claimed in any one of claims 1 to 35 and the assembly of glass sheet and interlayer with a layer of the adhesive composition therebetween is exposed to irradiation to cure the adhesive and bond the sheet and interlayer together.

38. A method as claimed in claim 36 or claim 37 in which the adhesive composition is photopolymerisable and the irradiation is by ultra-violet light.

39. A laminate comprising a first sheet of glass bonded to a second sheet which is selected from glass sheets and clear plastics sheets by means of a layer of a composition as claimed in any one of claims 1 to 35 which has been cured by irradiation.

40. A laminate comprising a clear plastics foil or film interlayer one face of which is bonded to a glass sheet and the other face of which is bonded to a second sheet selected from glass sheets and clear plastics sheets and wherein at least the bond between the interlayer and the glass sheet is by means of a layer of a composition as claimed in any one of claims 1 to 37 which has been cured by irradiation.

41. A radiation-curable liquid adhesive composition substantially as hereinbefore described with reference to any one of the Examples.

42. A method of producing a clear glass laminate substantially as hereinbefore described with reference to any one of the Examples.



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

This Page Blank (uspto)